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Formaldehyde Synthesis For Laser Enhanced Radiocarbon Dating

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An experimental study has been performed of the photochemical conversion of carbon monoxide to formaldehyde using a low pressure mercury lamp. This represents one of the steps in applying the laser enrichment of carbon-14 to radiocarbon dating, an area of interest for the hydrogeological assessment of nuclear waste disposal sites. The dependence of conversion efficiency on lamp temperature, gas pressure and gas flow rate has been investigated.

INTRODUCTION

As part of Ontario Hydro's technical assistance program (TAP) to Atomic Energy of Canada Ltd (AECL) a research program was initiated in 1982 to investigate a method of improving the carbon dating of groundwater samples in connection with hydrogeological studies in the Canadian Shield/1/. The technique is based on pre-enrichment of the carbon-14 content by the selective laser dissociation of formaldehyde (H_2CO), which has the potential to improve the accuracy and increase the age limit of groundwater dating when combined with accelerator-based mass spectrometry (AMS) to count the carbon-14 atoms/2/. Details of an experimental study of the laser enrichment of carbon-14 have been reported earlier/3/.

Since the carbon in water samples appears as carbon dioxide (CO_2) or as a carbonate which can be readily converted to CO_2, a carbon dating process incorporating pre-enrichment requires a method of converting CO_2 to H_2CO/4/. The efficient conversion of CO_2 to carbon monoxide (CO) has already been demonstrated/5/. Therefore this report describes an experimental study of the conversion of CO to H_2CO in the presence of hydrogen using a mercury sensitized photochemical reaction in which a low pressure mercury lamp acts as the source of light.

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Experimental Procedure

The experimental layout is shown in Figure 1. The key component is a low pressure mercury lamp built in-house which consists of a 28 cm long, 25 mm diameter quartz envelope concentrically surrounding a 6 mm Vycor reaction cell. It is immersed in a temperature controlled water bath. The lamp is powered by a 600V 1.25A transformer connected to metal electrodes in series with a 3H 500 mA choke to stabilize the circuit. Normally the lamp runs at 300 mA.

After baking the lamp for several days at 150°C mercury was introduced along with 5 torr of neon. The latter is used to initiate the discharge and also improves efficiency and increases lamp life. Under normal operating conditions 50% of the electrical power consumed by the lamp is emitted as optical output at 253.7 nm. In our experiments this amounted to 27.5 W along the length of the reaction cell. Mercury also emits a strong line at 184.9 nm but the Vycor walls prevent this light from reaching the cell.

A heated reservoir filled with 5 cc of mercury is the source of Hg atoms which, after being excited by the ultraviolet light, participate in three-body collisions with carbon monoxide and hydrogen to generate formaldehyde, as discussed below.

Gas mixtures ($CO + H_2$) are metered into the system using a capacitance manometer. A bellows pump circulates the gases through the mercury reservoir and the reaction cell. Any condensible reaction products such as H_2CO are removed by a liquid nitrogen trap. The rate of gas circulation is controlled by a needle valve and monitored by the flowmeter. A 1 L buffer volume increases the total volume of the system and hence the amount of H_2CO product.

Reaction products were measured in two ways. One was a direct method based on the measurement of the decrease in pressure as the conversion took place. This was used in long irradiations which generated several torr of H_2CO. Short duration experiments did not give a sufficiently large change in pressure to be accurately measured by this method. Therefore, in these experiments the non-condensibles were pumped away and the amount of product was inferred from the pressure rise resulting from warming the liquid nitrogen trap to room temperature.

Results and Discussion

Preliminary measurements were performed with the lamp temperature at 25°C, as controlled by the water bath. Figure 2 gives the measured H_2CO production rate as a function of gas flow rate for a 200 torr CO/400 torr H_2 mixture. The maximum rate of conversion of CO to H_2CO is 8 x 10^{-2}% per minute at a flow of 3.35 L/min. Figure 2 also shows that increasing the lamp temperature to 43°C raised the production rate to nearly 10 x 10^{-2}% per minute, with the peak coversion occurring at

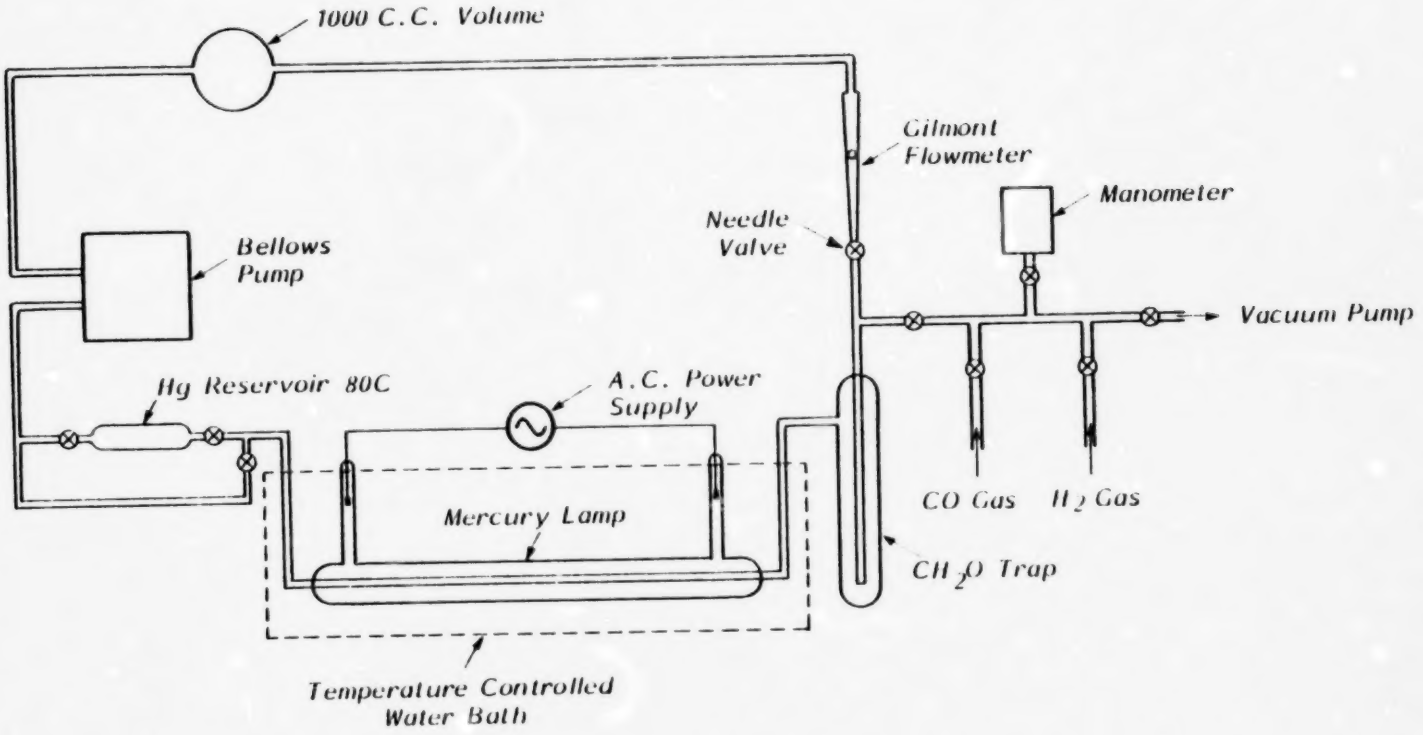

FIGURE 1

EXPERIMENTAL LAYOUT

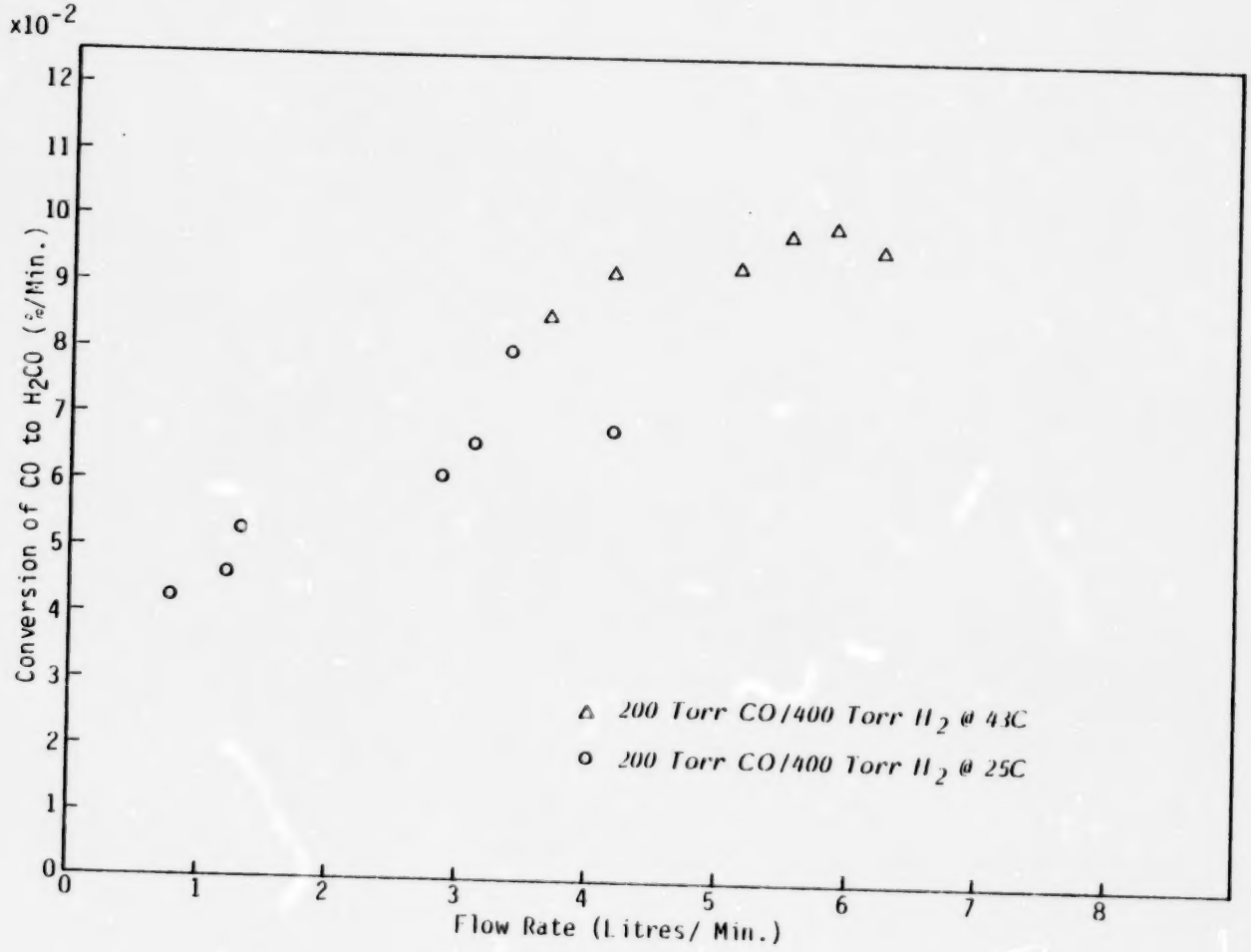

FIGURE 2

FORMALDEHYDE PRODUCTION AS A FUNCTION OF GAS FLOW RATE FOR TWO LAMP TEMPERATURES. DATA ARE BASED ON 10 MINUTE EXPERIMENTS.

higher flow (5.9 L/min). Other investigations of the performance of low pressure mercury lamps have also concluded that the optimum 253.7 nm output is obtained at temperatures near 40°C/6/. The optimum gas flow rate is expected to increase with lamp output since any formaldehyde created in the reaction cell can also be dissociated by the ultraviolet light unless the flow is adjusted to reduce the interaction time.

Figure 3 gives the results of a study in which the total gas pressure was varied while the $CO:H_2$ ratio was kept constant at 1:2. The rate of H_2CO production is found to increase with pressure in the range 450 to 900 torr. The maximum pressure was limited by the connectors used in the glassware system. The solid line in Figure 3 corresponds to a theoretical expression derived from the kinetics of the reaction which predicts that the conversion rate varies as the product of CO pressure and the square root of the H_2 pressure, divided by the square root of the total pressure/7/. This means that the reaction rate is proportional to the concentration of hydrogen atoms, which is consistent with a reaction mechanism involving the creation of HCO radicals by the reaction of CO with H atoms formed by collisions of H_2 molecules with excited mercury atoms/7/. The HCO radicals then combine to give either H_2CO and CO or glyoxal ($H_2C_2O_2$). The latter can be separated from formaldehyde by simple vacuum distillations. In the present experiments 15% of the observed conversion corresponds to glyoxal formation.

The discrepancy between the theoretical curve and the observed data at higher pressure may be due to the variation in gas flow rate with pressure for a given setting of the flow meter. The actual flow rate at 900 torr is 10% less than the flow at 450 torr and this may result in a lower conversion rate.

With a total pressure of 900 torr at 43°C the H_2CO production rate did not depend greatly on the gas mixture for CO pressures above 100 torr, as shown in Figure 4. The results indicate that in a formaldehyde synthesis experiment the rate of conversion would fall significantly only in the latter stages of the process when the CO pressure dropped below 50 torr. During the major part of the sythesis the conversion rate would remain constant at 0.125% per minute.

This was confirmed in a 6.5 hour experiment (Figure 5) starting with 325 torr of CO and 575 torr of H_2. The data points represent the measured percent conversion of CO to H_2CO as determined by pressure measurements at selected time intervals. The solid line is the expected rate of conversion of CO to H_2CO for a constant conversion rate of 12.45×10^{-2}% per minute. Such a conversion rate corresponds to a fraction 0.998755 of CO remaining after each minute. Therefore, after T minutes the fraction remaining is $(.998755)^T$ and the percent of CO converted to H_2CO is $[1-(0.998755)^T] \times 100$. Extrapolating this curve to 90% conversion gives a required irradiation time of 31 hours. This compares favorably with the 24 hour duration found in an earlier study using an order of magnitude higher ultraviolet intensity/8/.

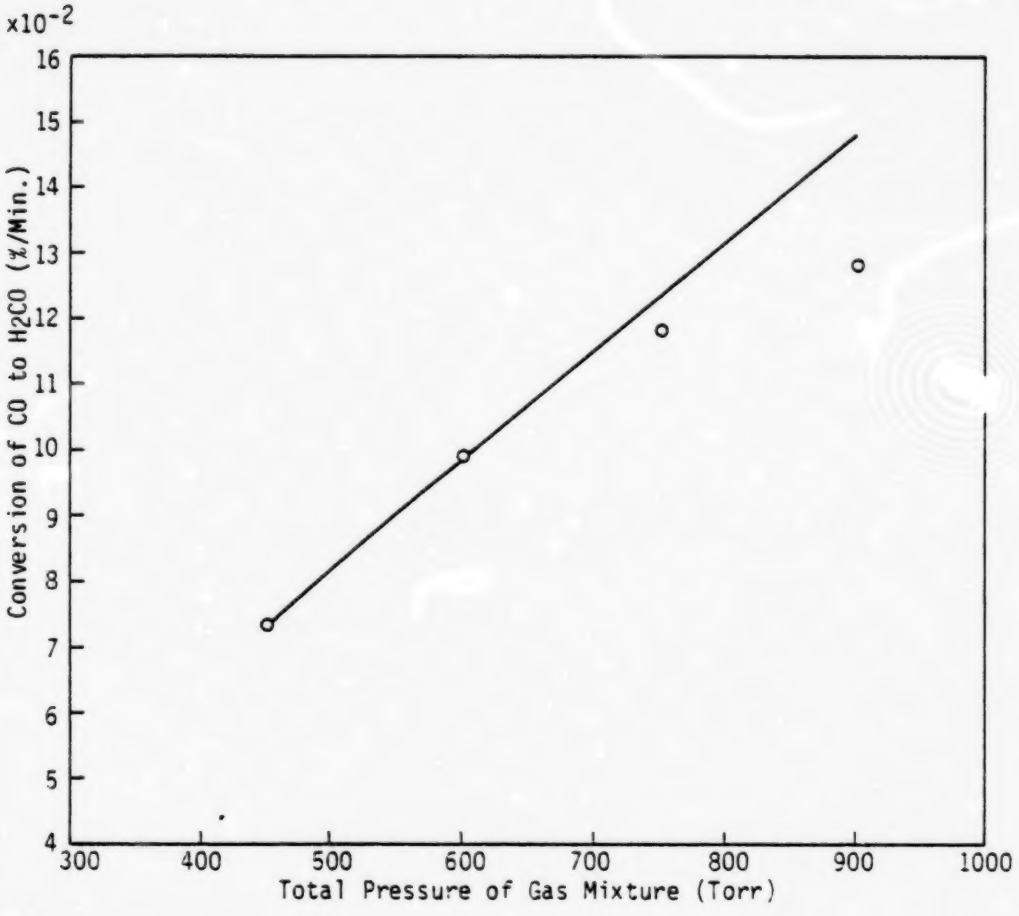

FIGURE 3

DEPENDENCE OF CONVERSION RATE ON TOTAL GAS PRESSURE FOR 1:2 CO:H_2 MIXTURES. RESULTS ARE FROM 10 MINUTE EXPERIMENTS WITH THE LAMP AT 43C.

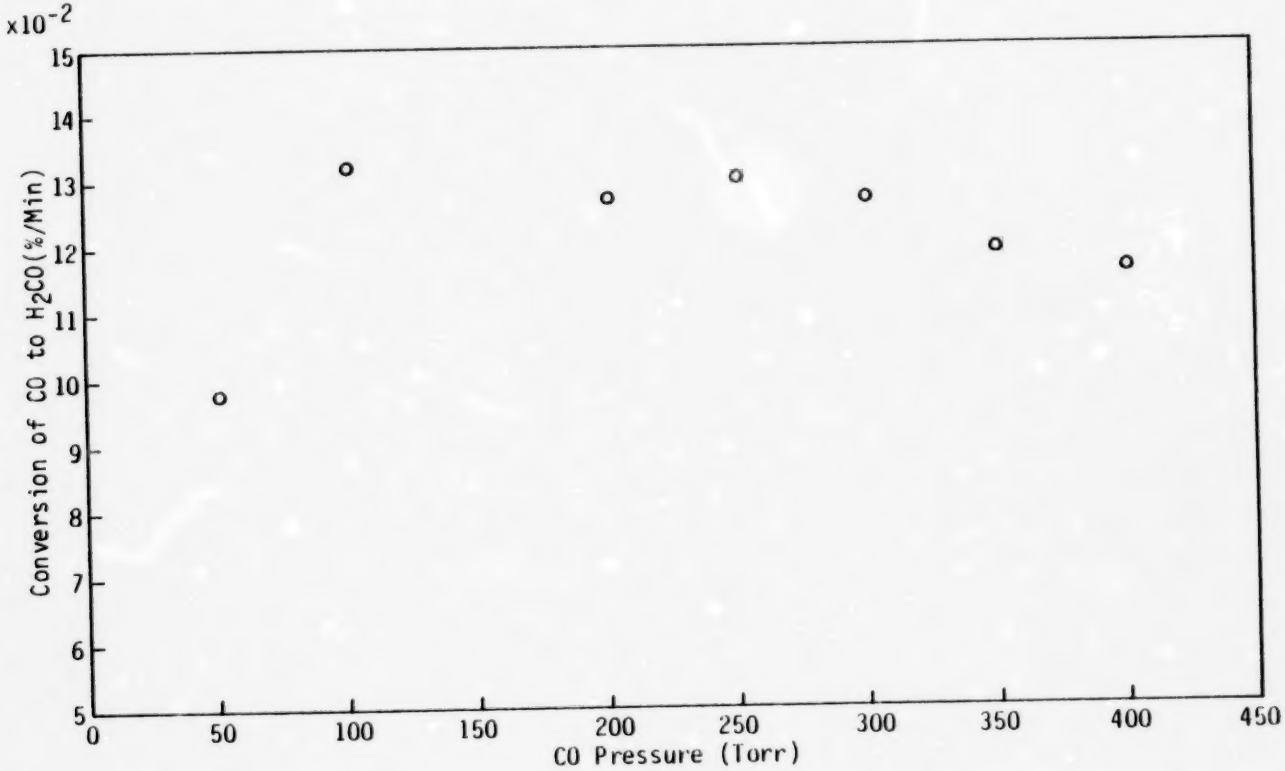

FIGURE 4

FORMALDEHYDE PRODUCTION AS A FUNCTION OF CO PRESSURE FOR A TOTAL GAS PRESSURE OF 900 TORR. RESULTS ARE FROM 10 MINUTE EXPERIMENTS WITH THE LAMP AT 43C.

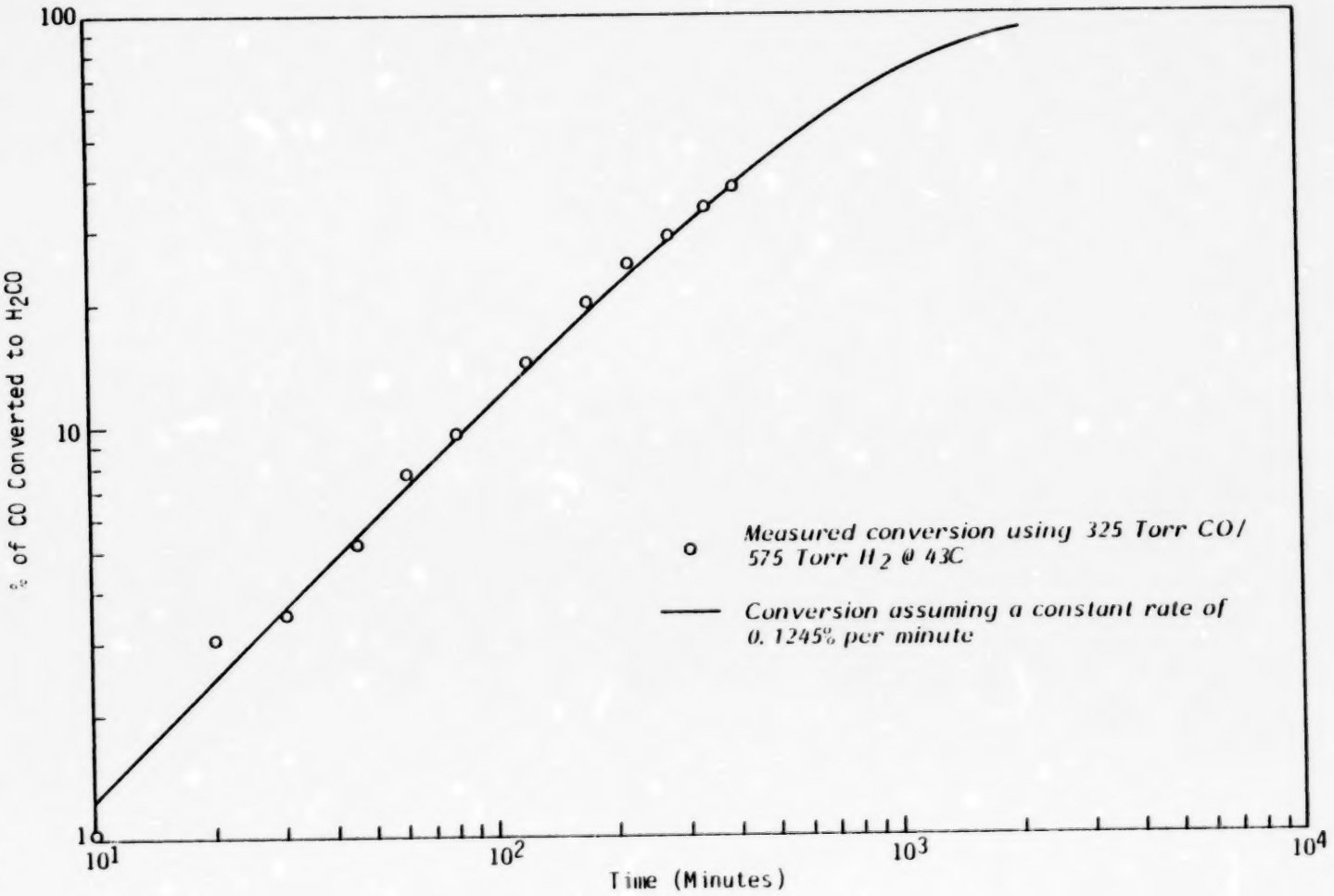

FIGURE 5

CONVERSION OF CO TO H_2CO DURING A 6.5 HOUR EXPERIMENT. THE SOLID LINE GIVES THE EXPECTED CONVERSION ASSUMING A CONSTANT RATE OF 12.45×10^{-2}% PER MINUTE.

The data of Figure 5 can be used to calculate how the duration of irradiation and the amount of formaldehyde produced depend on the volume of the apparatus (Figure 6). The present system has a volume of 1.2 L which is capable of generating 350 torr-L of formaldehyde in 31 hours. Such a curve would be useful in designing a formaldehyde synthesis facility for a specific application such as the groundwater dating project.

Improvements to the Design

As indicated by the data of Figure 3, a significant increase in the rate of conversion of CO to H_2CO could be achieved if higher gas pressures were used. The maximum CO pressure is limited by the vapour pressure of CO at liquid nitrogen temperatues, 450 torr. Since gas mixtures with a 2:1 ratio of H_2:CO appear to give good results, this corresponds to a total pressure of 1350 torr. A study of the dependence of conversion rate on the pressure would be required to determine the optimum total pressure.

Another way to improve conversion is to increase the output of the lamp at 253.7 nm. This could be accomplished by increasing the length and diameter of the lamp. Doubling the diameter would support four times the current while maintaining the same current density. Of course any increase in lamp output would require a corresponding increase in gas flow rate to prevent the photodissociation of formaldehyde product.

Summary

The synthesis of formaldehyde from carbon monoxide and hydrogen has been demonstrated using a low pressure mercury lamp constructed in-house. For the particular lamp and reaction cell used in this study a set of optimum parameters has been established which would yield a sample in a reasonable time period (31 hours). Improvements to the design could result in an order of magnitude reduction in the time required for formaldehyde synthesis.

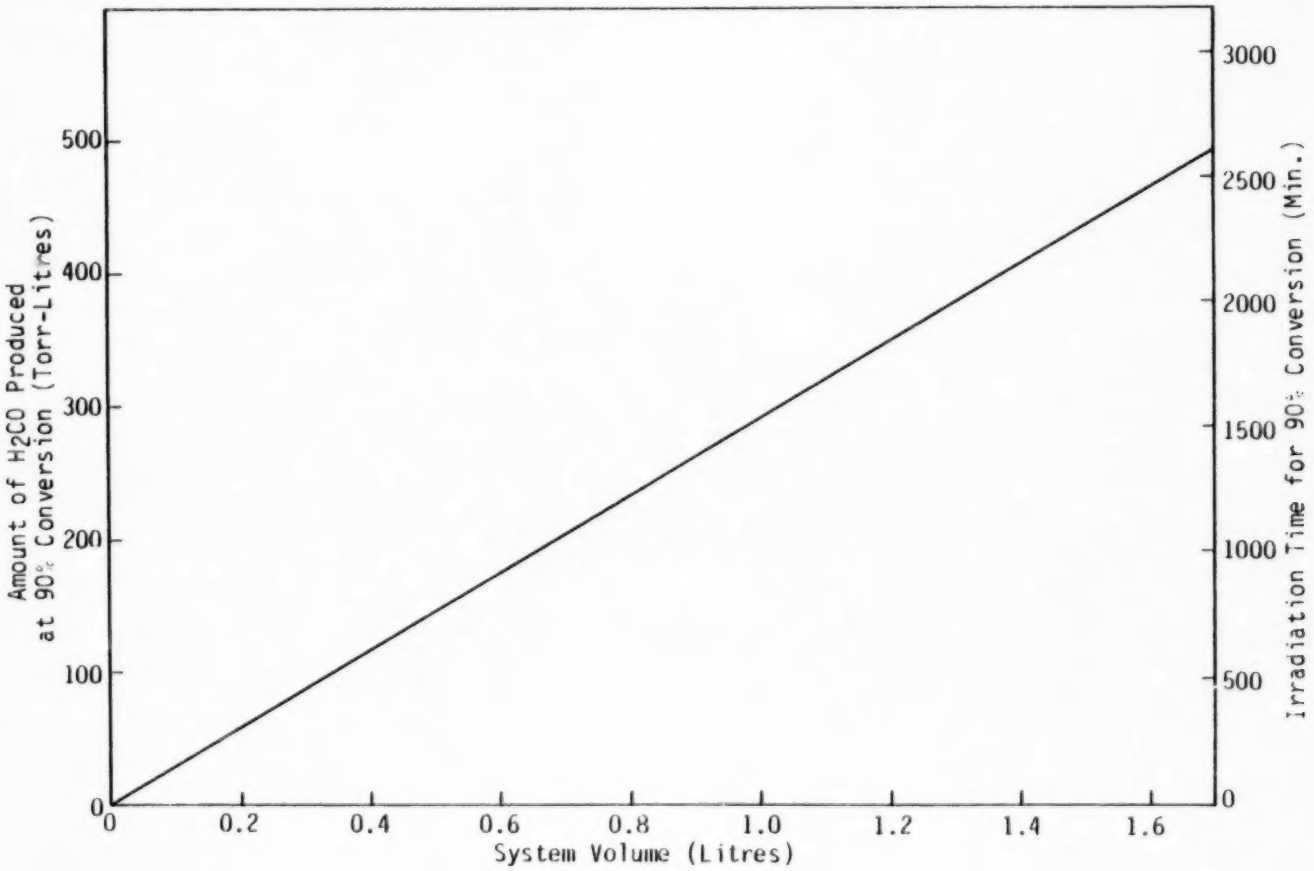

FIGURE 6

DEPENDENCE OF FORMALDEHYDE PRODUCT AND DURATION OF IRRADIATION FOR 90% CONVERSION ON VOLUME OF APPARATUS

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References

1. Mannik, L. "The Application of Lasers to Groundwater Dating". Research Report 82-510-K.

2. Hedges, R.E.M., P. Ho and C.B. Moore. "Enrichment of Carbon-14 by Selective Laser Photolysis of Formaldehyde". Applied Physics 23, 25 (1980).

3. Mannik, L. "Laser Enrichment of Carbon-14 for Groundwater Dating Applications". Research Report 84-197-K.

4. Woodall, K.B. "Sample Preparation Procedures for Laser Enhanced Radiocarbon Dating". Research Report 83-231-K.

5. Woodall, K.B. and J.R. Robins "Conversion of Carbon Dioxide to Carbon Monoxide for Carbon-14 Isotopic Enrichment". Research Report 83-476-K.

6. Elenbaas, W. in Fluorescent Lamps and Lighting (MacMillan, New York) p. 96 (1959).

7. Marshall, A.L., J.Phys. Chem. 30, 1634 (1926).

8. Marling, J.B., J. Chem. Phys. 66, 4200 (1977).